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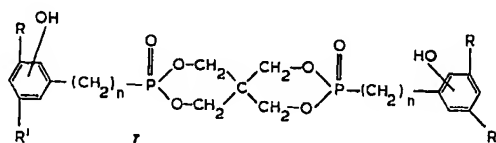
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PHOSPHONATE

(71) We, BORG-WARNER CORPORATION, of 200 South Michigan Avenue, Chicago, Illinois, United States of America, a corporation of the State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to novel hindered phenolic hydroxyl group containing phosphonates.

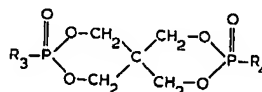
The phosphonates of the present invention have the formula:



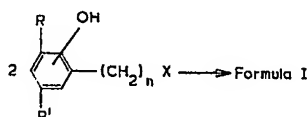
where each n independently is an integer of 1 to 4, each R independently is alkyl, hydrogen, cycloalkyl or aralkyl and each R' independently is alkyl, cycloalkyl or aralkyl. Thus each R independently, and each R' independently, may, for example, be alkyl of 1 to 20 or even 30 carbon atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec. butyl, t-butyl, t-amyl, amyl, hexyl, heptyl, octyl, 2-ethylhexyl, isooctyl, t-octyl, decyl, dodecyl, octadecyl, eicosyl, tetracosyl or triacontyl, cycloalkyl of 5 to 12 carbon atoms or more, e.g. cyclopentyl, cyclohexyl, methylcyclohexyl, cyclooctyl, cyclodecyl or cyclododecyl, or aralkyl of 7 to 36 carbon atoms or more, e.g. benzyl, 4-methylbenzyl, phenethyl, 6-phenylhexyl, 12-phenyldodecyl, 12- α -naphthyl dodecyl, 24-phenyltetracosyl, 30-phenyltriacontyl.

Preferably both R substituents and both R' substituents are alkyl, more preferably both R substituents and/or both R' substituents are tertiary alkyl, and most preferably both R substituents and both R' substituents are tertiary alkyl.

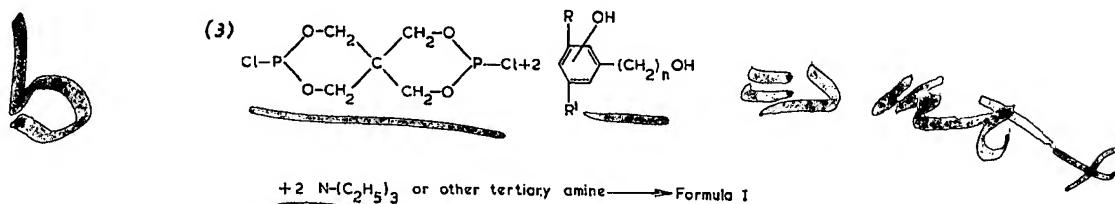
Examples of compounds within the present invention are 3,9-bis-(3,5-di-t-butyl-4-hydroxybenzyl) - 3,9 - dioxo - 2,4,8,10 - tetraoxa - 3,9 - diphospha - spiro(5,5) undecane; 3,9 - bis - (2 - (3,5 - dimethyl - 4 - hydroxyphenyl) - ethyl) - 3,9 - dioxo - 2,4,8,10 - tetraoxa - 3,9 - diphospha - spiro(5,5) - undecane; 3,9 - bis - (2 - hydroxy - 3 - t - butyl - 5 - methylbenzyl) - 3,9 - dioxo - 2,4,8,10 - tetraoxa - 3,9 - diphospha - spiro(5,5) - undecane. Other examples of compounds within the present invention are set forth in Table 1 below. The compounds in Table 1 have the formula:



Compound	R ₃	R ₄
1	3,5-di-t-octyl-4-hydroxybenzyl	3,5-di-t-octyl-4-hydroxybenzyl
2	3,5-di-n-octyl-4-hydroxybenzyl	3,5-di-n-octyl-4-hydroxybenzyl
3	3,5-di-t-butyl-4-hydroxybenzyl	3,5-di-t-amyl-4-hydroxybenzyl
4	3,5-di-dodecyl-4-hydroxybenzyl	3,5-di-dodecyl-4-hydroxybenzyl
5	3-eicosyl-4-hydroxybenzyl	3-eicosyl-4-hydroxybenzyl
6	3-triacontyl-4-hydroxybenzyl	3-triacontyl-4-hydroxybenzyl
7	3,5 - dicyclohexyl - 4 - hydroxybenzyl	3,5-dicyclohexyl-4-hydroxybenzyl
8	3 - cyclohexyl - 5 - ethyl - 4 - hydroxybenzyl	3-cyclohexyl-5-ethyl-4-hydroxybenzyl
9	3,5 - dicyclopentyl - 4 - hydroxybenzyl	3,5-dicyclopentyl-4-hydroxybenzyl
10	3 - methylcyclohexyl - 4 - hydroxybenzyl	3-methylcyclohexyl-4-hydroxybenzyl
11	3 - cyclododecyl - 4 - hydroxybenzyl	3-cyclododecyl-4-hydroxybenzyl
12	3,5-dibenzyl-4-hydroxybenzyl	3,5-dibenzyl-4-hydroxybenzyl
13	3 - benzyl - 5 - t - butyl - 4 - hydroxybenzyl	3-benzyl-5-t-butyl-4-hydroxybenzyl
14	3,5 - di - t - butyl - 2 - hydroxybenzyl	3,5-di-t-butyl-2-hydroxybenzyl
15	3,5-dihexyl-2-hydroxybenzyl	3,5-dihexyl-2-hydroxybenzyl
16	3,5 - dicyclohexyl - 2 - hydroxybenzyl	3,5-dicyclohexyl-2-hydroxybenzyl
17	4 - (3 - methyl - 5 - cyclohexyl - 4-hydroxyphenyl)-butyl	4 - (3 - methyl - 5 - cyclohexyl - hydroxyphenyl)-butyl
18	4 - (3,5 - di - t - butyl - 4 - hydroxyphenyl)-butyl	4 - (3,5 - di - t - butyl - 4 - hydroxyphenyl)-butyl
19	3 - (3,5 - di - t - octyl - 4 - hydroxyphenyl)-propyl	3 - (3,5 - di - t - octyl - 4 - hydroxyphenyl)-propyl
20	2 - (3,5 - di - t - butyl - 4 - hydroxyphenyl)-ethyl	2 - (3,5 - di - t - butyl - 4 - hydroxyphenyl)-ethyl
21	3,5-diethyl-4-hydroxybenzyl	3,5-diethyl-4-hydroxybenzyl



40



In the above formulae, R, R' and n are as previously defined, R₁ is alkyl, X is halogen (preferably chlorine or bromine), and R₂ is aryl such as phenyl or tolyl, or alkyl such as methyl, butyl, ethyl, isopropyl, hexyl or octyl. Any conventional alkaline catalyst can be used, for example, sodium hydroxide, potassium hydroxide, sodium methylate, sodium phenolate, sodium hexylate or potassium methylate.

Typical examples of starting materials for reaction (2) are diphenyl pentaerythritol diphosphite, dimethyl pentaerythritol diphosphite, diethyl pentaerythritol diphosphite, dibutyl pentaerythritol diphosphite, diisooctyl pentaerythritol diphosphite.

In procedure (1) R₁ can be any of the alkyl groups mentioned for R₂. However, R₁ cannot be an aryl group. Thus in reaction (1) there can be used dimethyl pentaerythritol diphosphite, diethyl pentaerythritol diphosphite, dibutyl pentaerythritol diphosphite, diisopropyl pentaerythritol diphosphite or dioctyl pentaerythritol diphosphite.

In procedure (3) the tertiary amine can be tripropylamine, tributylamine or diethylmethylamine. In reaction 3 when n is 1, the phosphonate is the only product. In reaction 3 when n is 2, 3 or 4, any phosphite formed can be rearranged to the phosphonate by adding a small amount of sodium iodide or potassium iodide, e.g. 1 to 10 mol % of the dichloropentaerythritol diphosphite.

As hindered phenols to be used as starting materials to make the final hindered mol phosphonates there can be used, for example, 3,5-di-t-butyl-4-hydroxybenzyl chloride, 3,5-di-t-butyl-4-hydroxybenzyl alcohol, 3,5-di-t-butyl-4-hydroxybenzyl bromide, 3,5-di-t-butyl-4-hydroxybenzyl iodide, 3,5-dimethyl-4-hydroxybenzyl chloride, 3,5-dimethyl-4-hydroxybenzyl alcohol, 4-(3-methyl-5-cyclohexyl-4-hydroxyphenyl)-butyl chloride, 4-(3-methyl-5-cyclohexyl-4-hydroxyphenyl)-butyl alcohol, 3,5-di-t-octyl-4-hydroxybenzyl bromide, 3-t-butyl-4-hydroxybenzyl chloride, 3-t-butyl-4-hydroxybenzyl alcohol, 3,5-di-n-octyl-4-hydroxybenzyl chloride (and the corresponding alcohol), 3,5-di-t-amyl-4-hydroxybenzyl alcohol (and the corresponding chloride), 3,5-didodecyl-4-hydroxybenzyl chloride (and the corresponding alcohol), 3-eicosyl-4-hydroxybenzyl alcohol (and the corresponding chloride), 3-triacontyl-4-hydroxybenzyl chloride (and the corresponding alcohol), 3,5-dicyclohexyl-4-hydroxybenzyl chloride (and the corresponding alcohol), 3-cyclohexyl-5-ethyl-4-hydroxybenzyl alcohol (and the corresponding chloride), 3,5-dicyclopentyl-4-hydroxybenzyl chloride (and the corresponding alcohol), 3-methylcyclohexyl-4-hydroxybenzyl alcohol, 3,5-dibenzyl-4-hydroxybenzyl chloride (and the corresponding alcohol), 3-benzyl-5-t-butyl-4-hydroxybenzyl alcohol (and the corresponding chloride), 2-hydroxy-3-t-butyl-5-methylbenzyl chloride (and the corresponding alcohol), 2-hydroxy-3,5-di-t-butyl-benzyl alcohol (and the corresponding chloride), 2-hydroxy-3,5-dihexylbenzyl chloride (and the corresponding alcohol), 4-(3,5-di-t-butyl-4-hydroxyphenyl)-butyl alcohol (and the corresponding chloride), 2-(3,5-di-t-butyl-4-hydroxyphenyl)-ethyl alcohol (and the corresponding chloride).

If mixed products are desired such as that of compounds 1 of Table 1, there can be used a mixture of starting phenols.

The hindered phenol phosphonate compounds of the present invention are useful as phenolic antioxidants. Thus they can be used to stabilize organic materials normally subject to oxidative deterioration.

The phenolic phosphonate antioxidant is used in an amount of 0.005 to 10 parts per 100 parts of the polymer or other material to be stabilized, preferably 0.1 to 5 parts per 100 parts of polymer. Thus they are useful with many different kinds of solid polymers. For example, they can be used with resins made from vinylidene compounds such as vinyl chloride, vinylidene chloride, vinyl chloroacetate, chlorostyrenes, vinyl bromide and chlorobutadienes.

Such vinylidene compounds may be polymerized alone or in admixture with each other or with vinylidene compounds free from halogen. Among the halogen free materials which can be copolymerized with the halogen containing vinylidene compounds, e.g. vinyl chloride, are vinyl esters of carboxylic acids, e.g. vinyl acetate, vinyl

- propionate, vinyl butyrate and vinyl benzoate, esters of unsaturated acids, e.g. alkyl and alkenyl acrylates such as methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate and allyl acrylate as well as the corresponding methacrylates, e.g. methyl methacrylate and butyl methacrylate, vinyl aromatic compounds, e.g. styrene, p-ethylstyrene, divinylbenzene, vinyl naphthalene, α -methylstyrene, p-methylstyrene, dienes such as butadiene and isoprene, unsaturated amides such as acrylamide, methacrylamide and acrylanilide and the esters of α,β -unsaturated carboxylic acids, e.g., the methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, allyl, methallyl and phenyl esters of maleic, crotonic, itaconic and fumaric acids. Specific examples of such esters are diethyl maleate, dibutyl maleate and dibutyl fumarate.
- The copolymers in which at least 50% of the copolymer is made from a halogen containing vinylidene compound such as vinyl chloride, are among the preferred materials treated according to the invention.
- The antioxidants or stabilizers of the present invention are also effective when intimately mixed with halogen-containing resins in which part or all of the halogen is introduced into a preformed resin, e.g. chlorinated polyvinyl acetate, chlorinated polystyrene, chlorinated polyethylene, chlorinated polyvinyl chloride, chlorinated natural and synthetic rubbers and rubber hydrochloride.
- Typical examples of copolymers include vinyl chloride vinyl acetate (95:5 weight ratio), vinyl chloride-vinyl acetate (87:13 weight ratio), vinyl chloride-vinyl acetate-maleic anhydride (86:13:1 weight ratio), vinyl chloride-vinylidene chloride (95:5 weight ratio), vinyl chloride-diethyl fumarate (95:5 weight ratio) and vinyl chloride-trichloroethylene (95:5 weight ratio).
- The resin, e.g. polyvinyl chloride, can either be plasticized or unplasticized. As the plasticizer there can be employed conventional materials such as dioctyl phthalate, octyl decyl phthalate, tricresyl phosphate, 2-ethylhexyl diphenyl phosphate, dodecyl dicresyl phosphate, tributyl acetyl citrate, dioctyl sebacate and dibutyl sebacate. The plasticizer is used in conventional amount, e.g. 10 to 100 parts for each 100 parts of the vinyl chloride containing resin.
- There can also be incorporated 0.1 to 10 parts per 100 parts of the halogen-containing resin of a metal salt stabilizer. Thus, there can be used barium, strontium, calcium, cadmium, zinc, lead, tin, magnesium, cobalt, nickel, titanium and aluminium salts of phenols, aromatic carboxylic acids, fatty acids and epoxy fatty acids.
- Examples of suitable salts include barium di(nonylphenolate), strontium di(nonylphenolate), strontium di(amyphenolate), barium di(octylphenolate), strontium di(octylphenolate), barium di(nonyl-o-cresolate), lead di(octylphenolate), cadmium-2-ethylhexoate, cadmium laurate, cadmium stearate, zinc caprylate, cadmium caproate, barium stearate, barium-2-ethylhexoate, barium laurate, barium ricinoleate, lead stearate, aluminium stearate, magnesium stearate, calcium octoate, calcium stearate, cadmium naphthenate, cadmium benzoate, cadmium p-tert. butylbenzoate, barium octyl salicylate, cadmium epoxy stearate, strontium epoxy stearate, cadmium salt of epoxidized acids of soybean oil, and lead epoxy stearate.
- In plastisol formulations there can also be included from 0.1 to 10 parts per 100 parts of resin of an epoxy vegetable oil such as epoxidized soybean oil or epoxidized tall oil.
- The antioxidants of the present invention are particularly effective with solid unsaturated hydrocarbon polymers such as polyethylene, polypropylene, polybutene, ethylene propylene copolymers (e.g. 50:50, 80:20 and 20:80), ethylene-monoolefin copolymers wherein the monoolefin has 4-10 carbon atoms and is present in a minor amount, e.g. ethylene-butene-1 copolymer (95:5) and ethylenedecene-1 copolymer (90:10). Furthermore, they can be used to stabilize natural rubber, styrene-butadiene rubber (SBR rubber), e.g. (75% butadiene-25% styrene), EPDM rubbers, ABS terpolymers (e.g. 20-30% acrylonitrile, 20-30% butadiene, 40-60% styrene), polyisoprene, polybutadiene, styrene-acrylonitrile copolymers, butyl rubber, polyacrylonitrile and acrylonitrile copolymers (e.g. acrylonitrile-vinyl chloride 85:15), polystyrene, impact modified polystyrene, butadiene-acrylonitrile (e.g. 60:40); polymerized acrylates and methacrylates, e.g. polymethyl acrylate, polymethyl methacrylate and polybutyl acrylate, polyacetals, e.g. polyoxymethylene polymers (e.g. Delrin and Celcon), polycarbonates (e.g. bisphenol A-carbonate polymer), polysulfones, polyphenyleneoxides, phenoxy resins, epoxy resins, A-epichlorhydrin, nylon, cellulose acetate, cellulose acetate-propionate, cellulose acetate butyrate, cellulose nitrate, polyethylene oxide, ethyl cellulose, linear polyesters, e.g. polyethylene terephthalate (Dacron, Mylar), unsaturated polyester, e.g. vinyl compounds modified alkyls such as ethylene glycol phthalate-maleate modified with styrene or diallyl phthalate, oil modified alkyl resins, e.g. soybean oil-glyceryl phthalate resin, chlorosulfonated polyethylene,

polyurethanes (e.g. toluene diisocyanate reaction products with polypropylene glycol molecular weight 2025 or with glycerine-ethylene oxide adduct having a hydroxyl number of 56). (The words "Delrin", "Dacron" and "Mylar" are registered Trade Marks).

As the EPDM rubber there can be employed many of the commercially available EPDM rubbers. The EPDM rubber normally contains 30 to 70 molar percent (preferably 50 to 60 molar percent) of ethylene, 65 to 20 molar percent (preferably 35 to 45 molar percent) propylene and 1 to 15 molar percent (preferably 3 to 5 molar percent) of the nonconjugated polyolefin. Usually the polyolefin is not over 10 molar percent. The ethylene and propylene can each be 5 to 95 molar percent of the composition.

As used in the present specification, the term "nonconjugated polyolefin" includes aliphatic nonconjugated polyene hydrocarbons and cycloaliphatic nonconjugated polyene hydrocarbons, e.g., endocyclic dienes. Specific examples of suitable nonconjugated polyolefins include pentadiene-1,4; hexadiene-1,4; dicyclopentadiene, methyl cyclopentadiene dimer, cyclododecatriene, cyclooctadiene-1,5; 5-methylene-2-norbornene.

Specific examples of suitable terpolymers are the Royalenes which contain 55 mole percent ethylene, 40 to 42 mole percent propylene and 3 to 5 mole percent dicyclopentadiene, Enjay terpolymers, e.g. ERP-404 of Enjay and Enjay 3509 which contains about 55 mole percent ethylene, 41 mole percent propylene and 4 mole percent 5-methylene-2-norbornene; Nordel, a terpolymer of 55 mole percent ethylene, 40 mole percent propylene and 5 mole percent hexadiene-1,4. (The word "Nordel" is a registered Trade Mark). Another suitable terpolymer is the one containing 50 mol percent ethylene, 47 mole percent propylene and 3 mole percent 1,5-cyclooctadiene (Dutrel).

Examples of EPDM rubbers are given in United States Patents 2,933,480; 3,000,866; 3,063,973; 3,093,620; 3,093,621 and 3,136,739, in British Patent 880,904 and in Belgian Patent 623,698.

There can also be incorporated in the hydrocarbon polymers, e.g. polypropylene, conventional additives such as phosphites in an amount of 0.1 to 10 parts per 100 parts of polymer. Typical of such phosphites are triphenyl phosphite, tris decyl phosphite, decyl diphenyl phosphite, di(p-t-butylphenyl) phenyl phosphite, di-phenyl-o-cresyl phosphite, trioctyl phosphite, tricresyl phosphite, tribenzyl phosphite, polymeric phosphites such as Weston 243-B (made in accordance with U.S. Patent No. 3,341,629) and prepared from triphenyl phosphite and hydrogenated bisphenol and having a molecular weight of about 3000 and Weston 440 (a linear polymeric pentaerythritol hydrogenated bisphenol A phosphite made in accordance with U.S. Patent No. 3,053,878, Weston WX 618-(distearyl pentaerythritol diphosphite), thiophosphites such as trilauryl trithiophosphite and tristearyl trithiophosphite. (The word "Weston" is a registered Trade Mark).

There can also be included thio compounds in an amount of 0.01 to 10%, usually 0.1 to 5% of the polymer. Thus, there can be used pentaerythritol tetra (mercaptoacetate), 1,1,1-trimethylolethane tri(mercaptoacetate), 1,1,1-trimethylolpropane tri(mercaptoacetate), dioleyl thiodipropionate, dilauryl thiodipropionate, other thio compounds including distearyl 3,3'-thiodipropionate, dicyclohexyl-3,3'-thiodipropionate, dicetyl-3,3'-thiodipropionate, dioctyl-3,3'-thiodipropionate, dibenzyl-3,3'-thiodipropionate, lauryl myristyl-3,3'-thiodipropionate, diphenyl-3,3'-thiodipropionate, di-p-methoxyphenyl-3,3'-thiodipropionate, didecyl-3,3'-thiodipropionate, dibenzyl-3,3'-thiodipropionate, diethyl-3,3'-thiodipropionate, lauryl ester of 3-methyl-mercapto propionic acid, lauryl ester of 3-butyl-mercapto propionic acid, lauryl ester of 3-lauryl-mercapto propionic acid, phenyl ester of 3-octylmercapto propionic acid, lauryl ester of 3-phenylmercapto propionic acid, lauryl ester of 3-benzylmercapto propionic acid, lauryl ester of 3-(p-methoxy)phenylmercapto propionic acid, lauryl ester of 3-cyclohexylmercapto propionic acid, lauryl ester of 3-hydroxy-methylmercapto propionic acid, myristyl ester of 3-hydroxy-ethylmercapto propionic acid, octyl ester of 3-methoxy-methylmercapto propionic acid, dilauryl ester of 3-carboxy-methylmercapto propionic acid, dilauryl ester of 3-carboxy-propylmercapto propionic acid, dilauryl-4,7-dithiasebacate, dilauryl-4,7,8,11-tetrathiotetradecandioate, dimyristyl-4,11-dithiatetradecandioate, lauryl - 3 - benzothiazylmercapto propionate. Preferably the esterifying alcohol is an alkanol having 10 to 18 carbon atoms. Other esters of beta thiocarboxylic acids set forth in U.S. Patent No. 2,519,744 can also be used.

Likewise, there can be included 0.01—10%, usually 0.1—5% of a metal salt stabilizer in the monoolefin polymer formulations. Examples of such salts are calcium stearate, calcium 2-ethylhexoate, calcium octoate, calcium oleate, calcium ricinoleate, calcium myristate, calcium palmitate, calcium laurate, barium laurate, barium stearate,

magnesium stearate as well as zinc stearate, cadmium laurate, cadmium octoate, cadmium stearate and the other polyvalent metal salts of fatty acids set forth previously.

There can also be added conventional phenolic antioxidants in an amount of 0.01—10%, preferably 0.1—5%. Examples of such phenols include 2,6-di-*t*-butyl-*p*-cresol (Ionol), butylated hydroxyanisole, propyl gallate, 4,4'-thiobis(6-*t*-butyl-*m*-cresol), 4,4'-cyclohexylidene diphenol, 2,5-di-*t*-amyl hydroquinone, 4,4'-butylidene bis(6-*t*-butyl-*m*-cresol), hydroquinone monobenzyl ether, 2,2'-methylene-bis(4-methyl-6-*t*-butylphenol) (Catalin 14), 2,6-butyl-4-decyloxy-phenol, 2-*t*-butyl-4-dodecyloxyphenol, 2-*t*-butyl-4-octadecyloxyphenol, 4,4'-methylene-bis(2,6-di-*t*-butyl phenol), *p*-aminophenol, *N*-lauryloxy-*p*-aminophenol, 4,4'-thiobis(3-methyl-6-*t*-butylphenol), bis[*o*-(1,1,3,3-tetramethylbutyl)phenol] sulfide, 4-acetyl- β -resorcylic acid, A stage *p*-*t*-butylphenolformaldehyde resin, crotonaldehyde condensate of 3-methyl-6-*t*-butylphenol, 2,6-di-*t*-butyl *p*-cresol (Topanol CA), 2,2-methylene bis 4-ethyl-6-*t*-butylphenol (AO-425), 4-dodecyloxy-2-hydroxy-benzophenone, 3-hydroxy-4-(phenylcarbonyl)-phenyl palmitate, *n*-dodecyl ester of 3-hydroxy-4-(phenylcarbonyl) phenoxy-acetic acid, *t*-butylphenol, octadecyl-(3,5-di-*t*-butyl hydroxyphenyl) propionate (Irganox 1076). (The words "Ionol", "Catalin", "Topanol", "AO" and "Irganox" are registered Trade Marks).

Epoxy compounds in an amount of 0.01—5% in the hydrocarbon polymer compositions can also be included. Examples of such epoxy compounds include epoxidized soya bean oil, epoxidized lard oil, epoxidized olive oil, epoxidized linseed oil, epoxidized castor oil, epoxidized peanut oil, epoxidized corn oil, epoxidized tung oil, epoxidized cottonseed oil, epichlorhydrinbisphenol A resins (epichlorhydrin-diphenylolpropane resins), phenoxy-propylene oxide, butoxy propylene oxide, epoxidized neopentylene oleate, glycidyl epoxystearate, epoxidized α -olefins, epoxidized glycidyl soyate, dicyclopentadiene dioxide, epoxidized butyl tallate, styrene oxide, dipentene dioxide, glycidol, vinyl cyclohexene dioxide, glycidyl ether of resorcinol, glycidyl ether of 1,5-dihydroxynaphthalene, epoxidized linseed oil fatty acids, allyl glycidyl ether, butyl glycidyl ether, cyclohexane oxide, 4-(2,3-epoxypropoxy) acetophenone, mesityl oxide epoxide, 2-ethyl-3-propyl glycidamide, glycidyl ethers of glycerine, pentaerythritol and sorbitol, and 3,4-epoxy-cyclohexane-1,1-dimethanol bis-9,10-epoxystearate.

The phenolic phosphonates of the invention can also be used to stabilize lubricating oils, e.g. aliphatic esters such as di-(2-ethylhexyl)-azelate and pentaerythritol tetracaprate; animal and vegetable derived oils, e.g., linseed oil, fat, tallow, lard, peanut oil, cod liver oil, castor oil, palm oil, corn oil and cotton seed oil; hydrocarbon material such as gasoline, both natural and synthetic diesel oil, mineral oil, fuel oil, drying oil, cutting fluids, paraffin, waxes and resins, and fatty acids such as soaps. The stabilizer in such cases can also be used in an amount of 0.005 to 10% of the material to be stabilized.

Unless otherwise indicated all parts and percentages, throughout this specification, are by weight. The following Examples illustrate the invention.

Example 1

3,9-Bis(3,5-di-*t*-butyl-4-hydroxybenzyl)-3,9-dioxo-2,4,8,10-tetraoxa-3,9-diphospha-spiro(5,5)undecane

One mole (256 g.) of 3,9-dimethoxy-2,4,8,10-tetraoxa-3,9-diphospha-spiro(5,5)-undecane was dissolved in 1 liter of toluene and 2 mols (509 g.) of 3,5-di-*t*-butyl-4-hydroxybenzyl chloride in 500 ml heptane were added. The mixture was heated slowly to 100—110°C. and methyl chloride was allowed to distil off. After 3 hours at 100°C. methyl chloride evolution had ceased and a heavy precipitate had separated. The mixture was cooled and filtered. The filter cake was washed with toluene to give 600 g. (90%) of the title compounds as a colorless, crystalline, high-melting solid.

Example 2

One mol (166 g.) of 2-(3,5-dimethyl-4-hydroxyphenyl)-ethyl alcohol was mixed with 128 g. (0.5 mol) of 3,9-dimethoxy-2,4,8,10-tetraoxa-3,9-diphospha-spiro(5,5)-undecane. Five grams of sodium methylate was added and the mixture was heated slowly to 150°C. Methanol started to distil off at 100°C. and in 2 hours 0.95 mol of methanol was recovered. Five grams of sodium iodide was then added and the mixture was heated for 10 hours at 150°C. At the end of this period a test with iodine showed the absence of trivalent phosphorus. The product was a colorless solid which was recrystallized from toluene. Infrared spectrum and phosphorus analysis were in agreement with the compound: 3,9-bis[2-(3,5-dimethyl-4-hydroxyphenyl)ethyl]-3,9-dioxo-2,4,8,10-tetraoxa-3,9-diphospha-spiro(5,5)undecane.

Example 3

3,9-Bis(2-hydroxy-3-t-butyl-5-methylbenzyl)-3,9-dioxo-2,4,8,10-tetraoxa-3,9-diphospha-spiro(5,5)undecane

One mol (256 g.) of 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphospha-spiro(5,5)undecane dissolved in 1 liter of toluene was added to 384 g. (2 mols) of 2-hydroxy-3-t-butyl-5-methylbenzyl alcohol dissolved in 500 ml of toluene. Two hundred grams (2.05 mols) of triethylamine were added to the benzyl alcohol solution. The chloride solution was added to the amine-alcohol solution with cooling. When the addition was complete, the mixture was heated to 80°C. and filtered hot from the amine hydrochloride. Upon cooling, 520 g. (92%) of a colorless, crystalline solid was recovered. A phosphorus analysis and infrared spectrum confirmed the compound to be consistent with the title compound.

Example 4

Unstabilized polypropylene powder (Hercules Profax 6501) was thoroughly blended with 0.5% of the compound of Example 1 to produce a stabilized polypropylene. (The words "Hercules" and "Profax" are registered Trade Marks). Blending can be accomplished in any suitable manner, e.g., in a Banbury mixer.

Stability can be tested in any conventional manner, e.g. using the oven aging test and the Fadeometer test described in U.S. Patent No. 3,714,300, col. 5, lines 23—48. (The word "Fadeometer" is a registered Trade Mark).

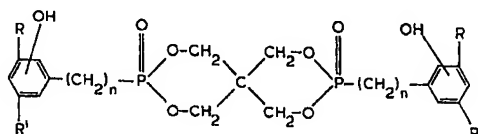
Example 5

100 parts of unstabilized polypropylene powder (Hercules Powder 6501) were thoroughly blended with 0.2 parts of the compound prepared in Example 2 and 0.5 part of dilauryl thiodipropionate to obtain a stabilized polypropylene.

The phenolic phosphonate compounds of the present invention also act as flame and fire retardants for solid hydrocarbon polymers such as polyethylene, polypropylene, polyisoprene, butadiene-styrene copolymer, EPDM polymers and ethylene-propylene copolymer.

WHAT WE CLAIM IS:—

1. A compound having the formula



where each R independently is hydrogen, alkyl, cycloalkyl or aralkyl, each R' independently is alkyl, cycloalkyl or aralkyl and each n independently is an integer of 1 to 4.

2. A compound according to claim 1 wherein each R independently is hydrogen, alkyl of 1 to 30 carbon atoms, cycloalkyl of 5 to 12 carbon atoms or aralkyl of 7 to 36 carbon atoms.

3. A compound according to claim 1 wherein both R substituents are other than hydrogen.

4. A compound according to claim 3 wherein each R independently is alkyl of 1 to 20 carbon atoms and each R' independently is alkyl of 1 to 20 carbon atoms.

5. A compound according to claim 4 wherein the OH groups are in the 2 and 2' positions.

6. A compound according to claim 4 wherein the OH groups are in the 4 and 4' positions.

7. A compound according to claim 4 wherein both R substituents are t-butyl.

8. A compound according to claim 7 wherein both R' substituents are t-butyl.

9. A compound according to claim 7 wherein each n is 1.

10. A compound according to claim 4 wherein each n is 1.

11. A compound according to claim 1 wherein each n is 1.

12. A compound having the formula:

